

Growth Kinetics of the Homogeneously Nucleated Water Droplets: Simulation Results

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Abstract. The growth of homogeneously nucleated droplets in water vapor at the fixed temperatures $T = 273, 283, 293, 303, 313, 323, 333, 343, 353, 363$ and 373 K (the pressure $p = 1$ atm.) is investigated on the basis of the coarse-grained molecular dynamics simulation data with the mW-model. The treatment of simulation results is performed by means of the statistical method within the mean-first-passage-time approach, where the reaction coordinate is associated with the largest droplet size. It is found that the water droplet growth is characterized by the next features: (i) the rescaled growth law is unified at all the considered temperatures and (ii) the droplet growth evolves with acceleration and follows the power law.

1. Introduction

Nucleation is one of the possible ways, by means of which a phase transition can be initiated. According to the classical nucleation theory, it is assumed that nucleus (cluster) of a new phase becomes stable to grow in a ‘mother phase’, when its size reaches some critical value – the critical size n_c . Consequently, both related processes, nucleation and nuclei growth, belong to the initial stages of phase transition. The character of phase transition depends directly on the nucleation rate J_s and the growth rate G . Appearance of liquid droplets (bubbles) as origins of condensation (vaporization) and emergence of crystallite grains at crystallization are the typical examples of nucleation. A feature of homogeneous nucleation¹ for most of molecular systems at the natural conditions is that the characteristic spatial scale [1], which is associated with the linear critical size of the nucleated phase, takes the values $10^{-9} \div 10^{-7}$ m. Thereby, the processes of nucleation and of nuclei growth are excellent candidates to be studied by means of the methods of molecular dynamics simulation. However, the probabilistic character of nucleation (the values of nucleation rate, critical size, growth rate and others) prompts applying the statistical treatment of the simulation results.

Recently, it was shown that the mean-first-passage-time (MFPT) approach can be successfully used to define all the characteristics of nucleation kinetics from the data of molecular dynamics simulations [2, 3]. In the idealized case of the symmetric nucleation barrier, the MFPT-distribution obtained from the set of independent simulations or from experiments is interpolated in the nucleation regime by the error-function, and such parameters as the steady-state nucleation rate J_s (or the nucleation time scale $\tau_s = (J_s V)^{-1}$, V is the system volume), the critical size n_c and the curvature of the nucleation barrier associated with the Zeldovich factor

¹ Homogeneous scenario means the same probability for the nucleation event emergence over the whole system.

Z can be extracted by numerical fitting. An extended MFPT approach allows one to define all these parameters for a wider class of nucleation scenario by numerical analysis of the first derivative of the MFPT-curve with respect to the reaction coordinate (say, nucleus size). In the present work we show that the same MFPT-approach can be also applied to define the characteristics of the nuclei growth regime. We demonstrate this analysis as applied for the case of the water droplet growth.

2. Methods and results

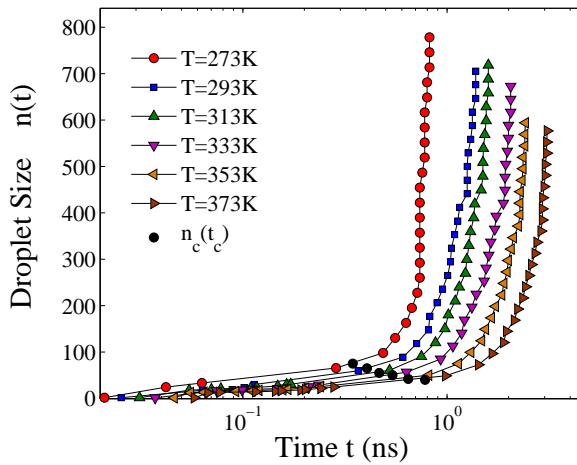


Figure 1. Growth curves of the nucleated water droplet as obtained from NpT -simulations within the MFPT-approach. The pressure is the same for all the considered cases, $p = 1$ atm. Black circles indicate the critical sizes n_c .

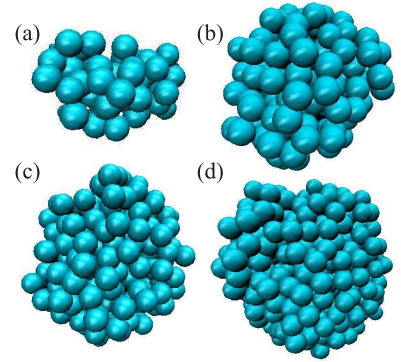


Figure 2. Water droplet at the temperature $T = 293$ K and at the different time after nucleation: (a) $n = 55$ molecules, $t(n) = 0.75$ ns, (b) $n = 123$ molecules, $t(n) = 0.83$ ns, (c) $n = 197$ molecules, $t(n) = 0.88$ ns, (d) $n = 308$ molecules, $t(n) = 0.91$ ns. Circles are the conventional symbols of water molecules.

The basic idea of the MFPT-approach is the next. First, it is necessary to focus on the reaction coordinate and to define the time scales of the first appearance of its values, $\tau(n)$. As a reaction coordinate for the case of the droplet nucleation, it is convenient to utilize the droplet size n , which defines the number of molecules (particles) involved in the nucleus of new (liquid) phase. Second, by defining these time scales from M independent ‘experiments’ and by averaging results, one obtains the MFPT-distribution:

$$\tau^{\text{MFPT}}(n) = \sum_{i=1}^M \tau_i(n).$$

In fact, the MFPT-distribution contains the information about nucleation and nucleus growth kinetics. For example, the first inflection points in the MFPT-curve defines the critical size n_c with the lag-time $t_c = \tau^{\text{MFPT}}(n_c)$ (for details, see [2]). Then, the part of the inverted MFPT-distribution $n(\tau^{\text{MFPT}})|_{n \geq n_c}$ corresponds to the most probable growth law of the nucleated droplet. Let us suppose the growth law in the following generalized form [4]:

$$n(t, t_c) = n_c + c_g \rho_c \mathcal{G}_c^{d\nu}(t - t_c)^{d\nu}, \quad (1)$$

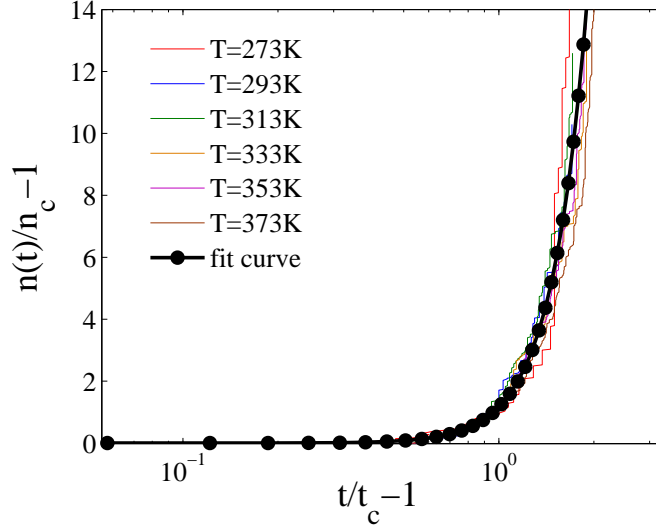


Figure 3. Rescaled growth curves at the different temperatures $T \in [273; 373]$ K (the pressure $p = 1$ atm); t_c is the lag-time of the droplet with the critical size n_c . Full circles correspond to the fit (see text for details).

where c_g is the shape-factor, ρ_c is the density of the nucleated phase, ν is the growth exponent – it is equal to unity in the case of constant growth rate, \mathcal{G}_c is the growth parameter and d is the system dimension. Without losing the generality in such a definition, the growth rate can be time-dependent term and takes the next form : $G(t) = \nu \mathcal{G}_c^\nu t^{\nu-1}$ (see also Ref. [1]). By fitting equation (1) to the distribution $n(\tau^{\text{MFPT}})_{|n \geq n_c}$, one can extract the values of the growth characteristics.

Molecular dynamics NpT -simulations were performed with the coarse-grained mW-model [5] of water vapor at the temperatures $T = 273, 283, 293, 303, 313, 323, 333, 343, 353, 363$ and 373 K at the pressure $p = 1$ atm.² For an each (p, T) -point the set from 100 independent runs at the identical initial conditions was carried out, and the time evolutions of the largest nucleated (liquid) droplet were stored for every run. Identification of liquid clusters was performed on the basis of the cluster analysis with the Stillinger rule [6, 7].

Figure 1 shows the growth curves of water droplet at the different temperatures. These results are obtained from molecular dynamics simulations within the MFPT-approach. The MFPT-treatment of these results reveals the interesting features of the nucleation-growth kinetics. The critical size $n_c(T)$ has a weak decay with the temperature (for the considered temperature range and the fixed pressure), that contradicts the classical nucleation theory predictions [1]. On other hand, the lag-time t_c increases with temperature from $t_c(T = 273 \text{ K}) = 0.69$ ns to $t_c(T = 373 \text{ K}) = 1.56$ ns. The nucleated droplets have shapes, which are closed to spherical ones (see figure 2). Further, the growth parameter \mathcal{G}_c decreases with temperature from $\mathcal{G}_c(T = 273 \text{ K}) = 576 \text{ m}^\nu/\text{s}$ to $\mathcal{G}_c(T = 373 \text{ K}) = 242 \text{ m}^\nu/\text{s}$, whilst the growth exponent is independent on the temperature and takes the value $\nu = 1.3$. This indicates on the next time dependence of the growth rate: $G(t) \sim t^{0.3}$. Other result is that the growth curves rescaled to

² The initial configurations were obtained by the isobaric cooling from the equilibrated vapor at the temperature $T = 900$ K and at the pressure $p = 1$ atm.

the form

$$\frac{n(t)}{n_c} - 1 = \frac{c_g \rho_c (\mathcal{G}_c t_c)^{3\nu}}{n_c} \left(\frac{t}{t_c} - 1 \right)^{d\nu}$$

are independent on the temperature and collapse onto a single growth curve (see figure 3).

3. Conclusions

The following results are presented in this work.

(i) The treatment of the experimental data and of the simulation results on the nucleation-growth kinetics can be performed on the basis of the MFPT-approach, which allows one to extract the main characteristics of the cluster growth process.

(ii) The growth of water droplets was studied on the basis of coarse-grained molecular dynamics simulations for a wide range of the temperature.

(iii) It is found that the rescaled growth law of water droplets within the mW-model is unified at all the considered temperatures.

(iv) It is established that the droplet growth evolves with acceleration and follows the power law.

References

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